

IMPROVED MULTILAYER BARRIER POLYMERIC FILMS**Field of the Invention**

The present invention relates to improved multilayer
5 barrier polymer films, to polymer compositions used in
the production of such films, and to a process for
producing the same.

Background of the Invention

10 The use and manufacture of polymer films is well
known. However, a single-layered polymer film, produced
from one polymer composition, may not have the properties
desired by the user of the film, or may lack additional
desirable properties, e.g., impermeability to oxygen or
15 other gases, and may need to be laminated for sealing and
humidity protection. This is a problem, for instance, in
the food-packaging industry.

One way to obtain desired properties is to make a
multilayer or laminated film. Two or more polymer
20 compositions are melted and laid together through
coextrusion, extrusion coating or a combination thereof,
to give a multilayer "tape" with either a planar or a
tubular form. After cooling, such tape is reheated and
stretched to give the film its final thickness and to
25 cause "orientation", a physical alignment of the polymer
macromolecules to improve mechanical properties. Shrink
films are manufactured in this way. Orientation can be
achieved in various ways, for example by bubble or tenter
frame techniques.

30 In multi-layer films, each layer of the film
contributes some of the desired properties. For example,
a film may have a thick outer layer to impart strength
and puncture resistance, another layer that is a barrier

to the passage of oxygen which might improve or increase the lifetime of a packaged food, and still another layer that improves the sealability of the film.

The properties attainable by multilayer films as
5 described above are limited by the fact that some layers with desired properties do not bind adequately to other layers. This is often a problem with gas-barrier layers. For instance, one could consider making a barrier shrink-film by sandwiching a brittle nylon or EVOH gas-barrier
10 layer between two polyethylene layers which are puncture resistant and sealable. However, polyethylene and nylon or EVOH do not bind to each other to form a three-layered film. Although this problem can sometimes be solved by careful formulation of polymer and additives (for
15 instance as taught in US Patent Nos. 4,778,715 or 5,114,795), it is appreciated by the skilled person that it is desirable to retain as much freedom as possible in designing the formulation of each layer.

One solution to this problem is the coextrusion of a
20 bonding-layer (also called a tie-layer) between the two layers, which do not bind to each other, as discussed in US 4,087,587. Thus, for instance, one could coextrude a grafted maleic anhydride layer, such as Admer™ (ex Mitsui), which binds well to both nylon (EVOH) and
25 polyethylene, between the two nylon (EVOH)-polyethylene interfaces. Illustrative of this method are US Patent Nos. 4,640,852, 5,759,648 or 5,895,694. The disadvantage of this solution is that the coextrusion of an extra layer is expensive, regarding required raw materials and
30 extra equipment.

It is an object of the present invention to provide an improved multilayer polymer free of tie-layers.

It is a further object of the invention to provide new polymeric compositions which, when extruded, result in a layer with desired properties, and which have the ability to bind to contiguous layers.

- 5 Other purposes and advantages of this invention will become apparent as the description proceeds.

Summary of the Invention

- Polymer compositions in contiguous layers which
10 ordinarily do not bind to each other are made to bind by cross-linking of macromolecules in one of the said layers with macromolecules in another of said contiguous layers, due to the presence of an irradiation-sensitive, typically UV-sensitive, additive or additives in one or
15 more of the polymer compositions of said layers. After coextrusion the tape is irradiated with UV or other suitable radiation, so that the additives cause the formation of cross links between macromolecules both within each layer and between contiguous layers, leading
20 to binding of the contiguous layers without the need to resort to an additional bonding layer.

- According to a preferred embodiment of the invention there are further provided film precursors consisting of two or more polymer compositions which ordinarily do not
25 bind to each other when coextruded as films, but which can be bound to each other by irradiation of the coextruded tape, whereby an additive or additives present in both of the layers, can induce cross-linking of macromolecules in the contiguous layers.

- 30 According to a preferred embodiment of the invention the interlayer cross-linking eliminates the need for binding layers. The elimination of the binding layers simplifies the production process and thus substantially

lowers the equipment cost and of the final product price. It also saves the costs of the binding layers. The inter-layer cross-linking enables multilayer films to be of higher quality if the total film thickness is
5 maintained.

According to a preferred embodiment of the invention the film precursors are used to manufacture shrink film, especially barrier shrink film. This barrier shrink film is suitable, and used for, food packaging.

10

Brief Description of the Drawings

Fig. 1 is a schematic representation of the double-bubble process;

Fig. 2 is a schematic illustration of a three-layer
15 film; and

Fig. 3 is a schematic illustration of a five-layer film.

Detailed Description of Preferred Embodiments

20 The production of a polymer film begins with the melting of a polymer composition followed by its extrusion through a die. This extrudate is further processed, e.g., by tenter drawing or double-bubble orientation, to impart to the polymer film its desired
25 thickness and properties.

In Fig. 1 the double-bubble technique for manufacturing a film is schematically illustrated. The polymer is melted in an extruder (2) which forces it through an annular die, while air is forced coaxially
30 through the die, to form a tube. The first bubble (3) is nipped closed at one end by the rolls (4). This is transported to an oven (7) that softens the polymer tube

sufficiently to allow stretching of the tape in the second bubble (8) to enhance film properties.

By using a coextrusion die, more than one layer can be simultaneously extruded, each layer with the same or a different polymer composition to form a multilayer film. In the case of the double-bubble technique, the die will typically be a coaxial annular die where the number of passageways is determined by the number of layers desired in the produced film. When two contiguous layers are chemically compatible, that is to say when they bind sufficiently well to each other when coextruded in their molten states, the film may be processed after extrusion in the same way as a single-layer film. The multilayered film so produced can be very useful, each layer contributing different desired properties.

However, incompatible layers must be bound together using an intermediate adhesive (or tie) layer. This need is obviated by the invention, through the exploitation of interlayer cross-linking. This is achieved by dissolving appropriate concentrations of one or more cross-linking photo-initiators in both of the polymer compositions which when melted and extruded are part of the multilayer tape. Thereafter, cross-linking is initiated to achieve the desired interlayer cross-linking.

In general, cross-linking can be achieved by any suitable technique, e.g., chemical, thermal or irradiation cross-linking. The skilled person will easily identify suitable cross-linking agents for the desired type of cross-linking. For example, cross-linking can be achieved by adding one of the common agents: N-hydroysuccinimide, glutaraldehyde, tosyl chloride, divinyl sulfone etc. However, according to a

preferred embodiment of this invention cross-linking is achieved by irradiation.

Cross-linking can also be achieved by irradiation with an electron beam. In this case, it is desirable to
5 incorporate a polymeric cross-linking enhancer (PCE) as taught in US 5,993,922. This patent teaches that PCE may consist, for example, of a polyene monomer, and a C₂-C₂₀ olefinic monomer.

As stated, according to a preferred embodiment of
10 the present invention cross-linking is achieved by irradiating the film. After extrusion, the multilayered tape is illuminated with the appropriate radiation (e.g., with electron-beam, gamma or UV radiation) to induce interlayer cross-linking.

15 According to another preferred embodiment of the invention, the cross-linking additives or the cross-linking initiators are sensitive to ultraviolet radiation and an ultraviolet oven or lamp is used to illuminate the film to induce interlayer cross-linking.

20 According to a still preferred embodiment of the invention, the film is produced using the double-bubble technique, and the ultraviolet oven or lamp is placed before the second bubble section of the line.

All the above and other characteristics and
25 advantages of the invention will be further explained through the following illustrative and non-limitative examples.

Example 1

30 It was desired to produce a less-expensive replacement for a five-layer state-of-the-art barrier shrink-film, described in Table 1 and illustrated in Fig. 2. The photoinitiator additive, 1% BP-L was added to

both the PE (polyethylene) (Dowlex 5056E ex, by Dow Chemical) and the EVOH (ethylene/vinyl alcohol) (G156B ex, By Kuraray), 10% of PCE (EPDM Vistalon 6505 ex Exxon) was added to each layer. EPDM is an ethylene-co-propylene elastomer. Unless otherwise specified, all percentages given herein are by weight. These two compositions were coextruded without tie layers (Table 2) through a coaxial annular extruder with three passageways installed in a double-bubble film production line.

Before passing through the heater preceding the second bubble section of the machine, the primary tube was irradiated by exposure to ultraviolet light. The primary tube thickness was 250 microns and it was irradiated by passage through the focal planes of 3 UV lamps from each side (total of 6 lamps), at a speed of 10 m/min. The lamps used were 240 W/cm, Nordson Quadcure providing a total dosage of 0.25 J per square centimeter in the UVC spectrum (which includes the 265 nm absorption line of benzophenone). The 25 microns film was obtained by orientation of the tube, after irradiation. This irradiation causes the molecules of the cross-linking additive to cross-link within and between each of the three layers, strongly binding the two outer polyethylene layers to the central EVOH layer. The produced three-layer barrier shrink-film described in Table 2 had properties equivalent to those of the five-layer shrink-film, especially with respect to oxygen permeability, at a significantly reduced cost of production.

Table 1

<u>Layer</u>	<u>Function</u>	<u>Composition</u>	<u>Material</u>
1	sealability and moisture barrier		Polyethylene
5 2	tie	Admer™	Anhydride modified polyethylene
3	gas barrier	EVOH	EVOH
4	tie	Admer™	Anhydride modified polyethylene
10 5	sealability and moisture barrier		Polyethylene

15 **Table 2**

<u>Layer</u>	<u>Function</u>	<u>Composition</u>
1	sealability and moisture barrier	Polyethylene + PI+PCE
2	gas barrier	EVOH + PI+PCE
20 3	sealability and moisture barrier	Polyethylene + PI+PCE

PI - Photoinitiator

PCE - Polymer Crosslinking Enhancer

25 **Example 2**

It was desired to produce a replacement for a seven-layer state-of-the-art superior barrier shrink-film, described in Table 3, where EVOH (ethylene-vinyl alcohol) serves as a gas barrier (as in Example 1) and a polyamide layer supports the EVOH orientation. The photoinitiator 1% BP-L and 10% PCE (as in Example 1) were added to both the polyethylene and the EVOH. The polyamide and the two polymer mixtures were coextruded through a coaxial

annular extruder with five passages installed in a double-bubble film machine. Before passing through the heater preceding the second bubble section of the machine, the tape was irradiated in an ultraviolet oven.

- 5 Irradiation conditions were the same as described in Example 1. This irradiation caused cross-linking within the four layers containing the photoinitiator and between the two polyethylene-EVOH interfaces, strongly binding the two outer polyethylene layers to the EVOH layers,
- 10 producing the five-layer barrier shrink-film described in Table 4 and illustrated in Fig. 3. Since polyamide binds well to EVOH, this five-layer film had properties equivalent to those of the seven-layer shrink-film with respect especially to oxygen permeability, at a
- 15 significantly reduced production cost.

Tabl 3

<u>Layer</u>	<u>Function</u>	<u>Composition</u>	<u>Material</u>
1	sealability, moisture barrier		Polyethylene
5 2	tie	ADMER™	PE/Maleic anhydride
3	gas barrier	EVOH	EVOH
4	gas barrier supports EVOH	Nylon, MXD-6	Polyamides
10	orientation		
5	gas barrier	EVOH	EVOH
6	tie	ADMER™	PE/Maleic anhydride
7	sealability, moisture barrier		Polyethylene
15			

Table 4

<u>Layer</u>	<u>Function</u>	<u>Composition</u>	<u>Material</u>
1	sealability, moisture barrier		PE+PI+PCE
20			Polyethylene
2	gas barrier	EVOH+PI+PCE	EVOH
3	gas barrier supports EVOH	Nylon, MXD-6	Polyamides
25	orientation		
4	gas barrier	EVOH+PI+PCE	EVOH
5	sealability, moisture barrier	PE +PI+PCE	Polyethylene

Example 3

This example demonstrates the important role of PCE presence and the irradiation effect. Three-layer systems (A/B/A) were prepared:

The first system contained polyethylene as layers A and EVOH as layer B. The polyethylene and the EVOH were the same as in Example 1. 1% PB-L was added then to each
 5 layer. PCE was not used.

System 2 had the same structure as System 1, but 10% PCE (EPDM) was added to each layer, as in Example 1.

The above systems were irradiated by UV. The primary tube thickness was 450 microns and it was irradiated by
 10 passing through the focal planes of 3 UV lamps from each side (total of 6 lamps), at a speed of 12 m/min. The lamps used were 240 W/cm, Fusion Inc., H bulbs, providing a total dosage of 0.25 J per square centimeter in the UVC spectrum (which includes the 265 nm absorption line of
 15 benzophenone).

The delamination force, i.e., the force required to separate the layers, is measured on the primary tube and summarized in Table 5 (results are in Newton/ 25 mm).

20	<u>System No.</u>	<u>Delamination Force</u>	
		Without Irradiation	Post Irradiation
	1	0.25	2
	2	0.5	15*

25 * No break in the interface. The break occurred in the PE layer.

While embodiments of the invention have been described by way of illustration, it will be understood that the invention can be carried out by persons skilled
 30 in the art with many modifications, variations and adaptations, without departing from its spirit or exceeding the scope of the claims.